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(56) Documents Cited
**GB 1123285 A GB 1096946 A GB 1045239 A
GB 1034154 A US 3740367 A**

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(54) **Method of preparing an aqueous dispersion**

(57) A process for the preparation for an aqueous dispersion of an ethylene/unsaturated carboxylic acid copolymer which comprises chemically comminuting the polymer in the presence of an aqueous alkaline solution of ammonium hydroxide or an amine or sodium hydroxide, whereby to provide the dispersed copolymer in neutralised form.

The dispersion is obtained using a shear disintegrator.

Novel process for preparing colloidal aqueous dispersions of high molecular weight Carboxylic acid functionalised Polyethylenes and Co Polymers, their application as film forming materials.

Polyethylene is highly regarded as a light stable Polymer having excellent mechanical properties coupled with good thermal and low temperature flexibility and barrier properties when applied as films.

Such fundamental properties are well understood and have been one of the considerations of this Polymer(backbone) for the manufacture of Acid functionalised Polyethylenes, specifically the Ethylene-Acrylic acid Co Polymer(EAA), Ethylene Methacrylic acid Copolymers and Ethylene maleicanhydride Copolymer. EAA in this text stands synonym for all types of Carboxy acid functionalised Polyethylenes

The EAA Copolymers are produced to improve certain properties of Polyethylene: Adhesion to polar and non polar surfaces of substrates, strength and toughness, puncture and tear resistance, low Temperature sealability, optical characteristics, haze and chemical resistance, eg, oil resistance.

Further derivatives are well known, the most important are salts, formed by neutralisation of the acid groups by cations like Alkali, Alkali earth, Zinc or Ammonia ions.

These improvements are due to the formation of phase separated ionic clusters in the continuous phase of the hydrophobic Polyethylene Polymer.

The major application of these Polyethylene Copolymers is in film extrusion, film blowing or film casting, especially in multi layer films for various applications.

Application of these Copolymers by extrusion or film blowing is limited by the film forming technology associated with extruders or melt calenders. A minimal thickness ie over 20 microns has to be applied in these continuous processes.

There is a demand to apply such Copolymers to substrates which should not be handled in the above film forming equipment, such as surfaces of wood, concrete, metal, textile or in a film thickness of lower than 20 microns, for example as a metal primer for coatings.

Methods used to apply films to the surfaces of the substrates mentioned above include application of solutions, dispersions or emulsions of the EAA Copolymers by spraying, dipping, brushing or bar coating.

In order to dissociate the ionic clusters and bring the EAA Polymer into solution, very strong solvents have to be used. The resulting concentration of EAA Copolymers in solution, which can be handled by the above process, is very low.

High concentrations of EAA Polymers in a liquid carrier can be achieved by an emulsification or dispersion process by partial or complete neutralisation of the acidic groups in EAA Polymers by cations, Ammonia or Amines. Use of water as solvent is an additional benefit and corresponds to new legislation on the use of volatile organic compounds (VOC)

Such aqueous Ammoniacal dispersions of EAA Polymers are known and commercially available. The (meth)acrylic acid or maleicanhydride content of these Copolymers is in the range 5 to 25 %

One major disadvantage with classic dispersions derived from macromolecules is often the incomplete disentanglement of the polymer chain. This can frustrate the ability to form continuous films or desired adhesion forces when applied by conventional techniques eg., atomised spray or bar coating. This is especially true when applying thick films ie dry film thickness (DFT) of over 100 microns.

These difficulties can be resolved using a pressure emulsification process, followed by freeze fracturing or shock cooling of the dispersed or emulsified particles. These processes contribute substantially to cost due to:-

The residence time in the processing equipment can be several hours and the associated energy inputs.

Material heating to 150 Deg.C or higher over several hours and shock cooling the resulting dispersion.

The particles produced using the pressure emulsification process normally have dimensions of between 30 to 300 microns.

It is an object of this invention to avoid the use of pressure emulsification processes and produce smaller and more uniform particles.

This application will demonstrate a novel and low cost process for preparing dispersions of EAA Copolymers by producing the colloidal dispersion by in-situ neutralisation of the acid groups of the Copolymers in the presence of Ammonia, using a disintegrator prior to rapid shearing forces, applied at ambient or slightly elevated Temperature.

High shear disintegrators, shear dispersors or shear emulsifying heads are known to those skilled in the art.

Shear is a type of deformation in which parallel planes in a body remain parallel but are relatively displaced in a direction parallel to themselves.

A disintegrator is a device based on a stator-rotor principle surrounded by a cylindrical shroud and fitted to the base of a drive capable of operating at revolutions ranging from 800 to 25,000 per min. Solid particles are retained within the shroud until repeated chopping reduces the individual particles to a size small enough to pass through a preset aperture into the body of the vessel and hence into a lower disintegrator head.

Once the particles have all passed through the upper head and shroud, repeated passages through both heads gives progressive shearing and comminution until a fine particle suspension or dispersion is obtained.

The distance between the rotor tip and the stator surface is within the range 25 - 100 microns. The surface texture of the stator is of a cast finish.

Suitable Ethylene (meth)acrylic acid or Ethylene maleicanhydride Copolymers for use in accordance with this invention contain about 10 to 25 % wt. of Acrylic acid. Methacrylic acid or Maleic Anhydride.

The EAA Copolymer can be introduced in the form of granules or powders. It can also be pumped above the softening or melting point of the Polymer in liquid form to the disintegrator head.

In a batch process, the disintegrator head is immersed in the aqueous solution of Ammonia or in solutions of Ammonia and /or Amines. The granules or powders of the Copolymers are introduced at a controlled rate into the vessel.

In a continuous process, the Copolymer granules or powder is blended in the liquid aqueous phase, the blend is then pumped directly into the disintegrator head. Alternatively, the

Copolymer is pumped in molten form to the head of the disintegrator.

The aqueous phase, before feeding it into the disintegrator head, can be at room Temperature or at elevated Temperature, for example, up to around 80 Deg.C. By the mechanical action of the disintegrator the Temperature will increase according to process conditions. The emulsification is immediate and the clarity of the dispersion is improved shortly after all the particles are charged and under shear action. The finished product displays a blue transparency and the typical particle size is approximately 35 nanometers (nm) when measured using a Coulter counter.

The acidic groups of the Copolymers, measured by the acid no., can be neutralised partially or completely, be it by Ammonia and or Amines.

Examples of Amines are: Aliphatic mono, di and tertiary amines, aminoalcohols.

The structure of the amines determine the evaporation rate and the odour of the dispersions.

The dispersions exhibit fast air drying rates.

Addition of metal cations in minor quantities to the Ammoniacal or amine containing dispersion can lead to cross linking of the resulting dry film, especially when the film is exposed to elevated Temperatures ie above 100 Deg.C

Plasticisers and low molecular weight plasticising resins, for example liquid ethylene vinyl acetate resins or maleinised low molecular weight Polybutadienes can be added to the dispersion for special effects. For example, the addition of maleinised Polybutadiene prevents cracking of the film in thick layers.

The Ammonium salt of the Copolymer acts as an emulsifier and dispersant for the additives. The dispersions are compatible with pigments, fillers and additives, for example, surfactants for lowering the surface tension of the aqueous solutions or dispersions.

The resulting Polymer film has exceptional adhesion to polar substrates, eg. metals, paper, polyamides, glass and Textiles. The Polymer films exhibit water resistance, grease, oil, solvent resistance and heat sealability. The Polymer films can be redispersed by a hot water jet.

In order that the invention may be well understood the following examples are given by way of illustration only.

Example

An aqueous dispersion was prepared from 225 grams Ethylene Acrylic acid Copolymer having a melt index of 100 grams/10 min. and 20 % Acrylic acid, 56 grams of 25 % aqueous Ammonium Hydroxide, 719 grams of deionised water.

The equipment used was a Silverson Duplex disintegrator / dissolver.

The deionised water plus NH₃ were charged to the vessel and stirrer started. The speed was increased to approximately 2000 rpm.

The Polymer, supplied in pelletised form was introduced slowly to allow a controlled rate through the disintegrator. The water Temperature was allowed to increase to 70 Deg.C

The emulsification was immediate and the clarity of the dispersion improved shortly after all the particles were charged and under shear.

The mass was held under constant shear at approximately 2000 rpm for 30 mins.

The finished product displayed a blue transparency and the average particle size, measured by Coulter counter was 35 nanometers.

The product compared favourably with properties obtained using a classical pressure process.

Comparative example: Pressure emulsification process

An aqueous emulsion was prepared from 244 grams of an Ethylene /Acrylic acid having a melt Index of 100 g/10 min. and Acrylic acid content of 20 % wt., 20.3 grams of 25% Ammonium Hydroxide and 735.7 grams of deionised water.

The emulsion was prepared in a stainless steel pressure vessel equipped with electrical heating jacket and internal mixer operating at 200 rpm., hot water transfer pump with metering device in accordance with the following procedure:-

CoPolymer charged to vessel followed by Ammonium Hydroxide. Vessel was heated over 108 mins. to 150 - 155 Deg.C (7 - 8 bar) Deionised water preheated to 90 Deg.C was introduced at the rate of 5 cc/min. Temperature was maintained at 150-155 Deg.C (8 bar) with mixer operating at min. 100 rpm.

The water transfer was completed at a time between 138 to 140 mins. after start of injection.

Mixing continued at 150-155 Deg.C for a further 84 mins. After 84 mins. mixing the heating jacket was removed and replaced with a cooling bath containing iced water. The Temperature was allowed to reduce from 150 Deg.C to 60 Deg.C within 2 mins. A further vessel containing iced water was applied when the vessel Temp. reached 60 Deg.C to continue the fast rate of heat transfer until the vessel Temperature reached 40 Deg.C.

Stirring was maintained at 100 rpm.

The header pressure in the vessel was relieved and contents removed.

The product had the following properties:-

Test apparatus Coulter N4 Version 9.1

SDP Intensity results

Mean particle dia. nm		50.1
S.D. (nm)		56
C.V. %		110
Size (nm)	S.D. (nm)	Amount %
30	3	84
153	24	16
Dust		0
Total solids content		24.43
pH	10.9	

Claims

M&C FOLIO: 230P66377

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CLAIMS:

1. A process for the preparation for an aqueous dispersion of an ethylene/unsaturated carboxylic acid copolymer which comprises chemically comminuting the polymer in the presence of an aqueous alkaline solution of ammonium hydroxide or sodium hydroxide, whereby to provide the dispersed copolymer in neutralised form.
2. A process as claimed in claim 1 in which the copolymer is a copolymer of ethylene and acrylic acid, methacrylic acid or maleic anhydride.
3. A method as claimed in claim 2 in which the copolymer is derived from a mixture containing from 10 to 25% by weight of the acrylic acid, methacrylic acid or maleic anhydride.
4. A method as claimed in claim 1 in which the resultant particles have a particle size of from 36 to 66 nanometers.
5. A method as claimed in claim 1 substantially as hereinbefore described with reference to the Example.

Patents Act 1977
Examiner's report to the Comptroller under Section 17
(The Search report)

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Relevant Technical Fields

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(ii) Int Cl (Ed.5) C08J 3/05

Search Examiner
DIANE DAVIES

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13 OCTOBER 1993

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Documents considered relevant following a search in respect of Claims :-
1-5

(ii) ONLINE DATABASES: WPI

Categories of documents

X: Document indicating lack of novelty or of inventive step.

P: Document published on or after the declared priority date but before the filing date of the present application.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

A: Document indicating technological background and/or state of the art.

&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
X	GB 1123285 A	(BAYER AG) Preparation of stabile latices by vigorous stirring in presence of alkali such as ammonia or NaOH	1-5
X	GB 1096946 A	(UNION CARBIDE CORP) Dispersions of ethylene/acrylate co-polymers by heating and stirring in an autoclave	1-5
X	GB 1045239 A	(W R GRACE & CO) Preparation of emulsion using a high speed air stirrer in presence of base	1-5
A	GB 1034154 A	(NAT DIST CHEM CORP) Dispersions of ethylene/acrylate polymers by high speed stirring under heat-alkali absent	
A	US 3740367 A	(DU PONT LTD) Colloidal dispersions of ammoniacal solutions of acrylate co-polymers by vigorous agitation	

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).